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# TECHNICAL NOTE

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SAMPLING STUDIES DOWNSTREAM OF HYDROGEN - NITROUS

OXIDE - DILUENT FLAMES

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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#### SUMMARY

Composition and temperature profiles were measured in the burned gas downstream of rich and lean  $\rm H_2\text{-}N_2\text{O}$  flames diluted with nitrogen, argon, and air. A cooled porous-plate burner was used. Temperatures were measured with coated fine-wire thermocouples, and chemical analysis was done mainly by mass spectrometry.

The nitric oxide (NO) yield from rich flames was independent of the pressure and initial equivalence ratio and increased with burned gas temperature. On this basis it was proposed that the NO was formed by the reaction

$$N_2O + H \rightarrow NO + NH$$

which is about 50 times slower than

$$N_2O + H \rightarrow N_2 + OH$$

and has an activation energy near 38 kilocalories.

Results for lean flames were based on the composition profiles of N<sub>2</sub>O, NO, O<sub>2</sub>, and H<sub>2</sub> in the burned gas. The sampling data indicated that the reaction N<sub>2</sub>O + O  $\rightarrow$  2NO has an activation energy considerably less than 3O kilocalories per mole and is about 2O times slower than N<sub>2</sub>O + O  $\rightarrow$  N<sub>2</sub> + O<sub>2</sub>. The contribution of thermal decomposition of N<sub>2</sub>O to the observed N<sub>2</sub>O decay was estimated to be negligible in the downstream zone.

The yield of NO downstream of lean flames depended on pressure and oxygen yield as well as temperature. The dependence observed was qualitatively explained on the basis that all three modes of  $N_2{\rm O}$  decay, reaction with hydrogen atoms, reaction with oxygen atoms, and thermal decomposition, were important in determining the rate of formation of NO within the flame.

#### INTRODUCTION

Chemical sampling in the nearly isothermal zone just downstream of flat flames has afforded a means of studying the rates of gas reactions at high temperatures (refs. 1 to 3). This report describes sampling measurements downstream of lean and rich  $\rm H_2\text{-}N_2O$  flames diluted with nitrogen, argon, or air. Measurements of temperature and composition were obtained over a wide range of experimental conditions and were correlated to obtain information on the reactions of  $\rm N_2O$  with hydrogen atoms and with oxygen atoms.

#### EXPERIMENTAL PROCEDURE

Flat flames were established on a cooled porous-plate burner 4 inches in diameter; this has been described previously (ref. 3). The burner was mounted in the base of a low-pressure chamber. Gas samples from the region just downstream of the flame were withdrawn through an uncooled quartz orifice probe set on a traversing device. The results were insensitive to the size of the orifice. Convenient sampling rates over the range of pressure studied were obtained with orifices about 25 microns in diameter.

Gas analysis was done with a mass spectrometer. (Some of the data, including all the results at 180 mm Hg, had been obtained prior to the acquisition of a mass spectrometer by gas chromatography. These earlier results were shown, by experimental checks, to be consistent with the later mass-spectrometer results.) The probe led directly to the mass spectrometer through a flexible connection. The sampling line and inlet system of the mass spectrometer were kept at a pressure no greater than 1/20 of the pressure in the combustion chamber, and the analysis itself was usually done at a pressure of about 70 microns. Temperatures were measured with platinum - platinum-13-percent-rhodium thermocouples made of wires 0.001 inch in diameter that were butt-welded together. The thermocouples were flame-coated with silica to reduce catalytic heating, and the readings were corrected for radiation.

Traverses across the burner surface showed a maximum temperature change of  $25^{\circ}$  K from one side to the other. Since the change was smooth and gradual, its effect could be minimized by taking all measurements near the burner center. Comparison of temperatures measured with several different thermocouples showed that results were almost always consistently better than  $\pm 10^{\circ}$  K and no worse than  $\pm 25^{\circ}$  K. Thermocouple traverses in the stream direction showed that, for all cases in which sampling measurements were made, the temperature change through the sampling zone was less than  $10^{\circ}$  K.

The burned gas was analyzed for  $\rm H_2$ ,  $\rm N_2$ , NO,  $\rm O_2$ , and  $\rm N_2O$ . Water was trapped out and estimated by difference. A sampling run generally consisted of 5 to 10 points taken at intervals of 0.5 to 1.5 millimeters. If the initial mixture was  $\rm H_2$  rich, however, the downstream reaction zone was adequately described by one or two sampling points because no N<sub>2</sub>O survived in the burned gas and the concentrations of the other species did not change significantly with distance.

For all rich mixtures studied, nitrogen was used as diluent in the ratio of roughly 1.4 moles of  $\rm N_2$  per mole of  $\rm N_2O$ . For fuel-lean mixtures, the diluent was either nitrogen, air, or, in a few cases, argon, in about the same proportions. This degree of dilution yielded a  $\rm N_2$  mole fraction in the burned gas of about 0.75 except for the few cases when argon was used. The initial  $\rm H_2/N_2O$  mole ratio was varied between 0.5 and 0.85; in most cases it was very close to 0.7. Temperatures obtained in the burned gas ranged from 1560° to 1950° K. Generally, temperatures with air dilution were 100° to 200° K lower than with nitrogen or argon dilution. Data were taken at pressure levels of 0.029, 0.058, 0.115, and 0.24 atmosphere (22, 44, 88, and 180 mm Hg). The pressure was read from a calibrated Wallace and Tiernan Precision Dial Manometer. At 22 and 44 millimeters of mercury the uncertainty in the pressure due to fluctuations was about  $\pm 0.5$  millimeter of mercury. At the two higher pressures the uncertainty was about  $\pm 1$  millimeter of mercury.

#### RESULTS AND DISCUSSION

#### Yield of Nitric Oxide From Fuel-Rich Flames

When the initial mixture contained a stoichiometric excess of  $\rm H_2$ , no  $\rm N_2O$  survived the flame reaction. However, in all cases a small quantity of NO was found downstream of the flame, a quantity which did not change with distance. The results are summarized in table I. Figure 1 shows a plot of the concentration of NO in the burned gas relative to the initial concentration of  $\rm N_2O$  as a function of temperature. The results show no effect of pressure change between 44 and 180 millimeters of mercury and no effect of initial equivalence ratio, which was varied between 1.1 and 1.6. (It was not possible to obtain data at pressures much lower than 44 mm Hg or equivalence ratios much larger than 1.6 because the flames were unstable under such conditions.) The amount of NO does increase slowly with temperature. If the change in NO yield depends on the shift of an equilibrium or on the change of a rate, the temperature dependence can be described by an energy of about 33 kilocalories per mole.

The fact that any measurable quantity of NO should survive the flame in the presence of  $\rm H_2$  is somewhat surprising. However, as shown in figure 1, a corresponding yield of NO was found downstream of a similar flame in the investigation of reference 4. The reaction responsible for the formation of NO within the flame is not immediately obvious. The main reaction for the disappearance of  $\rm N_2O$  in an  $\rm H_2\text{-}N_2O$  flame is

$$N_2O + H \rightarrow N_2 + OH$$
 (1)

for which the rate constant is given by (ref. 4)

$$k_{l} = 4 \times 10^{ll} e^{-\frac{16,300}{RT}}$$
 (liter/mole)(sec)<sup>-1</sup> (2)

where R is the universal gas constant and T is absolute temperature. Since the amount of NO produced is about 2 percent of the original N<sub>2</sub>O, it may be supposed that NO is formed by a second path for N<sub>2</sub>O decay that is about 50 times slower. Because the amount of NO is independent of pressure, the secondary reaction must be of the same molecularity as reaction (1). Furthermore, because it is independent of initial hydrogen concentration, and, therefore, of hydrogen concentration within the flame, the reacting species must be the same for both reactions. That is, the secondary reaction cannot occur between N<sub>2</sub>O and oxygen atoms produced by thermal decomposition of N<sub>2</sub>O, because, even if the N<sub>2</sub>O were able to compete with H<sub>2</sub> for the small concentration of oxygen atoms available, the concentration of oxygen atoms would be expected to vary strongly with the excess H<sub>2</sub> present.

These considerations suggest

$$N_2O + H \rightarrow NO + NH$$
 (3)

as the reaction leading to NO formation. If it is assumed that the yield of NO from the flame is proportional to the rate of the reaction producing it, then, from figure 1, it is seen that the activation energy must be about 49 kilocalories, that is, about 33 kilocalories greater than that required by reaction (1). Since reaction (3) is endothermic by only 25 kilocalories, it is energetically possible. If one postulates reaction (3) as responsible for NO formation, it would be desirable to trace the subsequent fate of the NH formed. It might be expected that NH would eventually be converted into ammonia. However, no ammonia was ever found as a stable product either in the downstream zone or on probing the flame zone itself. Thus, any NH formed by reaction (3) would have to be quickly destroyed and the ultimate product would be a species other than NH<sub>3</sub>. A possible path for NH destruction would be the reaction

$$NH + OH \rightarrow N + H_2O \tag{4}$$

which is exothermic by about 33 kilocalories.

## Nitrous Oxide Decay Downstream of

## Fuel-Lean Initial Mixtures

Sampling studies in the downstream zone are reported in reference 1 for fuel-lean flames at 1 atmosphere pressure between  $1450^{\circ}$  and  $1760^{\circ}$  K. The decay of N<sub>2</sub>O, the accumulation of NO, and the small, nearly steady concentration of residual H<sub>2</sub> were measured for initial mixtures with large amounts of added air (in effect, lean H<sub>2</sub>-air flames with added N<sub>2</sub>O). The sampling results were treated so as to give an estimate of the rate of the reaction

$$N_2O + O \rightarrow 2NO \tag{5}$$

in the downstream zone. From the results obtained by measurement in the downstream zone, the concentration of oxygen atoms in the flame zone itself was estimated. In the present work, attention has been directed entirely to the downstream zone.

Figure 2 shows several downstream composition profiles for flames with added  $N_2$  and added air as diluents (the added air acting partly as an oxidant). In figure 2, the distance scale is somewhat arbitrary, with zero taken roughly as the downstream edge of the flame. In all cases it was found that the rate of decay of  $N_2O$  with distance was much greater than the rate of increase of NO. The relative rates were about the same whether the flames contained added nitrogen or air. In all the cases examined, the relative changes of NO,  $N_2O$ , and  $O_2$  with distance satisfied the condition of conservation of mass for oxygen atoms.

Sampling profiles (fig. 2) were obtained at pressures of 22, 44, and 88 millimeters of mercury. At the two lower pressures the level of  $\rm H_2$  concentration was high enough to be accurately measured. At the highest pressure the measurement of  $\rm H_2$  concentration was considerably less accurate; nevertheless, the results are probably consistent to within 20 percent.

As is indicated in figure 2, the logarithm of the concentration of  $N_2O$  was linear with distance. Thus, the rate of decay with distance could be converted to a time rate of decay by the simple one-dimensional approximation (ref. 5)

$$-\frac{\mathrm{d} \ln[\mathrm{N}_2\mathrm{O}]}{\mathrm{d}t} = -\frac{\mathrm{d} \ln[\mathrm{N}_2\mathrm{O}]}{\mathrm{d}Z} v + D \left(\frac{\mathrm{d} \ln[\mathrm{N}_2\mathrm{O}]}{\mathrm{d}Z}\right)^2$$
 (6)

where t is time, Z is distance in the stream direction, v is a calculated stream velocity for the burned gas, and D is a calculated binary diffusion coefficient for  $N_2O$  diffusing into  $N_2$ . The same

diffusion coefficient was used regardless of the diluent in the initial mixture. The error introduced by this simplification is small.

An Arrhenius plot of all the N<sub>2</sub>O sampling data is shown in figure 3. For flames with added air, the level of O<sub>2</sub> in the burned gas was about five to seven times as great as with added N<sub>2</sub>. At constant pressure, both sets of data are correlated by  $\left[\text{O}_2\right]^{1/2}$ , where the value of oxygen concentration chosen for each sampling run is the maximum value found. Because the rate of increase of oxygen with distance is small, any other consistent choice would give the same result. This correlation shows that (1) the decay of N<sub>2</sub>O takes place by way of reactions (5) and (7)

$$N_2O + O \rightarrow N_2 + O_2$$
 (7)

(2) the change in the concentration of oxygen atoms in the sampling zone shows the same increase with temperature regardless of the level of  $O_2$  concentration, and (3) the contribution of collision-activated thermal decomposition of  $N_2O$  to the observed decay is negligible. The increase in  $[O_2]^{-1/2}$  d  $\ln[N_2O]/\mathrm{dt}$  with decreasing pressure indicates not only that the concentration of oxygen atoms is probably in excess of equilibrium, but also that the amount by which equilibrium is exceeded increases strongly as the pressure is reduced. A similar effect has been reported for  $H_2$  downstream of lean hydrogen-air flames (ref. 3).

The total temperature dependence of the  $N_2O$  decay, including both the activation energy for the  $N_2O$  reaction with oxygen atoms and the change in oxygen atom concentration with temperature is about 65 kilocalories per mole.

It can be shown that this temperature dependence requires that the rate of increase in oxygen atom concentration with temperature be smaller than the change corresponding to equilibrium. If  $N_2O$  decay takes place only by reactions (5) and (7), then the definitions

$$\frac{d \ln[N_2O]}{dt} = (k_5 + k_7)[O] = \kappa$$
 (8)

and

$$\frac{d \ln \kappa}{dT^{-1}} = \frac{d \ln(k_5 + k_7)}{dT^{-1}} + \frac{d \ln[0]}{dT^{-1}}$$
(9)

apply. Now, the first term on the right side of equation (9) equals at least 15/R, (ref. 6) or, possibly, about 30/R (ref. 1). If the equilibrium

$$[0] = K[0_2]^{1/2} \tag{10}$$

holds, then

$$\frac{\mathrm{d} \ln[0]}{\mathrm{d}T^{-1}} \approx \frac{61}{R} \tag{11}$$

and R d ln  $\kappa/\mathrm{dT}^{-1}$  must be about 75 to 90 kilocalories. This is larger than the observed value of 65 kilocalories and indicates that the change of oxygen atom concentration with temperature is less than the change corresponding to equilibrium. This behavior is consistent with most other pertinent observations (refs. 7 and 8).

The data at 22 millimeters of mercury show considerably more scatter than those at the higher pressures. Furthermore, there is some indication that the data with nitrogen dilution have a generally smaller temperature dependence than those with air dilution. Consideration of the sampling data as summarized in table II shows that, with  $N_2$  dilution  $[H_2]/[N_2]$  is four to five times as great at 22 as at 44 millimeters of mercury, whereas  $[O_2]/[N_2]$  is smaller by one-half to one-third. In fact, under these conditions the concentration of  $H_2$  is of the same order as that of  $O_2$ . Thus, for flames with nitrogen dilution at 22 millimeters of mercury, reaction (1) would be expected to attain some importance in the downstream zone; this circumstance would explain the observed effects.

Since the hydrogen concentration in the burned gas at several pressures is easily measurable, the concentration of oxygen atoms may be determined by the method given in reference 1. The reaction

$$H + H_2O \rightarrow OH + H_2$$
 (12)

is known to be equilibrated downstream of rich hydrogen-air flames (ref. 7). Assume that this steady state holds for lean flames as well. Since the forward and backward reactions

$$H + O_2 \neq OH + O$$
 (13)

are at least as fast as those of reaction (12) (ref. 1), the difference between equations (12) and (13)

$$H_2O + O \rightarrow H_2 + O_2$$
 (14)

is also balanced; the oxygen atom concentration is given by

$$[0] = K \frac{[H_2][o_2]}{[H_2O]}$$
 (15)

where K is the equilibrium constant for reaction (14). The values of  $[H_2]$  were computed from the level portions of the decay curves and, as before, the maximum values of  $[O_2]$  for each run were used.

It is possible that the concentration of  $\rm H_2$  in the sample does not correspond to that in the flame since the recombination of OH in the sampling line could change the amount of  $\rm H_2$  found. In reference 1, values of  $\rm k_5$  were measured that depended on knowledge of  $\rm [H_2]$ . Subsequently,  $\rm k_5$  was remeasured by a method that did not depend on  $\rm [H_2]$  (ref. 9). Good agreement was found, which suggested that the discrepancy between real and measured values was not serious. However, this point will be considered again after further analysis of the sampling results.

Figure 4 shows an Arrhenius plot of  $[0]^{-1}$  d  $\ln[N_20]/\mathrm{dt}$  for the data at 22, 44, and 88 millimeters of mercury. A satisfactory correlation is found between the runs with air dilution and nitrogen dilution at 44 and 88 millimeters of mercury. Once again, the data at 22 millimeters of mercury show considerable scatter. However, it is again apparent that the reaction taking place with nitrogen dilution is not entirely the same as for air dilution, and that probably, in the case of nitrogen dilution, there is a significant amount of reaction between nitrous oxide and hydrogen.

The results at 44 and 88 millimeters of mercury are correlated by

$$-\frac{1}{[0]}\frac{d \ln[N_20]}{dt} = 3 \times 10^{14} e^{-\frac{41,500}{RT}}$$
 (liter/mole)(sec)<sup>-1</sup> (16)

This expression is rather different from the one obtained from the rate of NO increase (refs. 1 and 9). Comparison with the values of  $\mathbf{k}_5$  in figure 4 indicates that the level of the rate constant is higher by a factor of about 40 and that the activation energy is about 13 kilocalories higher. In order to eliminate the effect of systematic error between different observers, values of  $\mathbf{k}_5$  were calculated in the present study from rates of NO increase. Only the data at 44 and 88 millimeters of mercury for flames with added air were used, since, in the other cases, the increase in NO concentration was too small for accurate measurement. The effect of diffusion was considered, in making the calculation, but because of the small rate of NO increase even with air addition, the effect had a negligible influence on the rate. Results for six runs, shown in figure 4, are correlated by

$$k_5 = \frac{d[NO]}{dt} \frac{1}{2[N_2O][O]} = 7 \times 10^{11} e^{-\frac{32,000}{RT}}$$
 (liter/mole)(sec)<sup>-1</sup> (17)

The values obtained are about twice as great as those reported in reference 9. The temperature dependence, however, yields an activation energy close to the reference 9 value of  $28\pm3$  kilocalories. On the basis of the discussion of the probable overall error in reference 9, the discrepancy

in the level of the rate constant is not serious. Thus, it appears that, based entirely on the present data, the rate of the reaction of  $N_2O$  with oxygen atoms, determined from  $N_2O$  decay, is still about 20 times as great as that determined from  $N_2O$  increase and furthermore has a slightly higher temperature dependence.

The significance of numerical quantities appearing in the rate expressions may be temporarily disregarded, so that consideration may be given only to the twenty-fold difference between the rates of  $N_2O$  decay and NO production. Two explanations for this difference are suggested. First, a part of the  $N_2O$  decay may occur by collision-activated unimolecular decomposition. This would explain the high value of both the rate and activation energy. However, the good correlation of the data with the square root of the oxygen concentration and the fact that the decay rate is independent of the pressure at constant oxygen atom concentration make it unlikely that this reaction is important. Further evidence can be offered that thermal decomposition is negligible. Table II shows that, near  $1700^{\circ}$  K, the decay rate of  $N_2O$ , expressed as d  $\ln[N_2O]/\mathrm{dt}$ , is about  $1000(\mathrm{seconds})^{-1}$ , the exact value depending on the oxygen concentration. A rough value of d  $\ln[N_2O]/\mathrm{dt}$  for the reaction

$$N_2O + M \rightarrow N_2 + O$$
 (18)

where M is the total gas concentration, can be calculated from the "limiting low concentration" expression derived in reference 10 from the data of reference 11. This expression is

$$-\frac{1}{[M]}\frac{d \ln[N_20]}{dt} = 4 \times 10^{12} e^{-\frac{59,000}{RT}}$$
 (liter/mole)(sec)<sup>-1</sup> (19)

At  $1700^{\circ}$  K and a pressure of 44 millimeters of mercury the value obtained for d  $\ln[N_20]/\text{dt}$  is about  $40(\text{seconds})^{-1}$ , which is practically negligible when compared with the total decay rate.

The other explanation would be that, as mentioned previously, the  $\rm N_2O$  decay takes place only by way of reactions (5) and (7), so that the observed decay rate gives the sum of the rates of (5) and (7). Because the total rate is much greater than the rates of (5) and (18), it corresponds approximately to the rate of (7). The observation that  $\rm k_7/k_5 \simeq 20$  is in strong disagreement with the results of reference 6. In that study, results for the initial stages of  $\rm N_2O$  decomposition near  $1000^{\rm O}$  K were interpreted by a proposed mechanism that accounted for the simultaneous rate of appearance of NO. By fitting their data to an expression derived from the mechanism, the authors of reference 6 inferred that  $\rm k_7/k_5 \simeq 0.4$ . The main argument in favor of the ratio obtained in this work would seem to be that, as soon as it is apparent that thermal

decomposition does not contribute significantly to the decay, simple inspection of the sampling data makes it apparent that  $\rm\,k_7>k_5$  .

With regard to the actual magnitudes of kinetic parameters, the preexponential factor in equation (17) is higher than the value expected for a bimolecular reaction by two or three orders of magnitude. (An alternative fitting of the data, which included all the results at 22 millimeters of mercury in the correlation, still gave a preexponential factor greater than  $10^{13}$ .) Thus, correspondingly, the activation energy found for reaction (7) should be too high. The most likely source of error would be a systematical temperature-dependent error in the determination of [0]. This could arise either from an invalid measurement of [ $H_2$ ] or from the failure of reaction (14) to be equilibrium. Then  $E_5$ , the activation energy for reaction (5), would also be too high, since it depends on the same values of [0] that were used to determine  $k_7$ . However,  $E_{5}$ , as presently determined, agrees with the value that was obtained in reference 1 by the same method and was later corroborated in reference 9 by a different method. Thus, the possibility appears that the true value of  $E_5$  is considerably less than the values in the range 28 to 32 kilocalories obtained in this work and in references 1 and 9.

# Yield of NO From Fuel-Lean Flames

The interpretation of the yield of NO downstream of fuel-lean flames is difficult because of several factors. First, the concentration of NO in the downstream zone increases with distance at a rate that depends on the initial mixture conditions. Therefore, it is difficult to describe the NO yield by a single value with much precision. By following the procedure used in the case of oxygen, the largest value of NO concentration found in any sampling run has been used to characterize the NO yield. Second, NO is formed in the flame by reaction with both hydrogen and oxygen. In order to obtain information about reactions (5) and (7), it is necessary to correct the total yield of NO for the amount formed by reaction (3). Thus, for an initial mixture containing  $\phi$  moles of  $\rm H_2$  per mole of N2O, the yield of NO due to reaction of N2O with O,  $\rm q_x$ , can be expressed by

$$q_{x} = \frac{q_{T} - \varphi q_{H}}{1 - \varphi} \tag{20}$$

where  $q_T$  and  $q_H$  are the total NO yield and the yield from reaction of  $\rm N_2O$  with H, respectively. Equation (20) assumes that the stoichiometric amount of  $\rm N_2O$  reacts with hydrogen atoms and the excess of  $\rm N_2O$  with oxygen atoms. However, it is difficult to obtain a valid estimate of  $\rm q_H$  because of the importance of transport effects within the flame, especially diffusion of hydrogen. Also, some correction must be made for thermal decomposition of N<sub>2</sub>O within the flame. As a first guess on  $\rm q_H$ , values obtained

from figure 1 might be used and thermal decomposition assumed to be negligible. However, these assumptions do not lead to a successful correlation of the data.

Values of the NO yield for various experimental conditions are given in table II. A fair correlation is obtained with the square root of the maximum downstream  $O_2$  concentration; this result suggests that the NO yield depends on the concentration of oxygen atoms in the flame zone. As shown in figure 5, a plot of  $\log([0_2]^{-1/2}[N0]/[N_20]_0)$  for lean flames is independent of oxygen concentration at any pressure but shows an inverse pressure dependence. The dependence of NO yield on oxygen concentration and pressure can be qualitatively explained on the basis that, within the flame, both reaction with oxygen atoms and thermal decomposition are important modes of decay for  $N_2\text{O}$ . The former process gives NO as a product; the latter does not. High pressure and low concentration of oxygen tend to decrease the oxygen atom concentration in the flame zone and increase the contribution of thermal decomposition to the total decay rate. This reduces the yield of NO. Conversely, a high yield of NO is favored by low pressure and high oxygen concentration. This explanation is compatible with the sampling results of the previous section because, even though the rate of thermal decomposition of  $N_2O$ is negligible when compared with the total  $N_2O$  decay rate, it is comparable to the rate of that mode of N2O decay producing NO.

At any pressure, the NO yield shows a temperature dependence that corresponds to an energy of about 14 kilocalories per mole. This can be qualitatively explained on the basis that NO is produced in the flame by both reactions (3) and (5). As noted previously, the NO yield from reaction (3) increases with temperature at a rate corresponding to 33 kilocalories. However, since the sampling results summarized in figure 4 indicate that  $E_7 > E_5$ , the NO yield from the reaction of N2O with O should decrease with increasing temperature. Thus, the total yield of NO from a flame in which both modes of NO production occur should increase with temperature at a rate corresponding to less than 33 kilocalories, as was observed.

### SUMMARY OF RESULTS

Composition and temperature were measured downstream of flat rich and lean hydrogen - nitrous oxide flames diluted with nitrogen, argon, and air. The following results were obtained:

l. Small amounts of nitric oxide were found downstream of fuel-rich flames. The correlation of yield data suggested that the origin of  ${\tt NO}$  is the reaction

$$N_2O + H \rightarrow NO + NH$$

2. The decay of N $_2{\rm O}$  downstream of lean flames was caused almost entirely by the reaction of N $_2{\rm O}$  with oxygen atoms. The contribution of thermal decomposition of N $_2{\rm O}$  was small. On this basis the reaction

$$N_2O + O \rightarrow N_2 + O_2$$

was about 20 times faster than

$$N_2O + O \rightarrow 2NO$$

and had a slightly higher activation energy.

3. The variation of the NO yield from lean flames with experimental conditions was explained on the basis that all three modes of  $N_2O$  decay, reaction with oxygen atoms, reaction with hydrogen atoms, and thermal decomposition, contributed significantly to  $N_2O$  consumption within the flame.

Lewis Research Center
National Aeronautics and Space Administration
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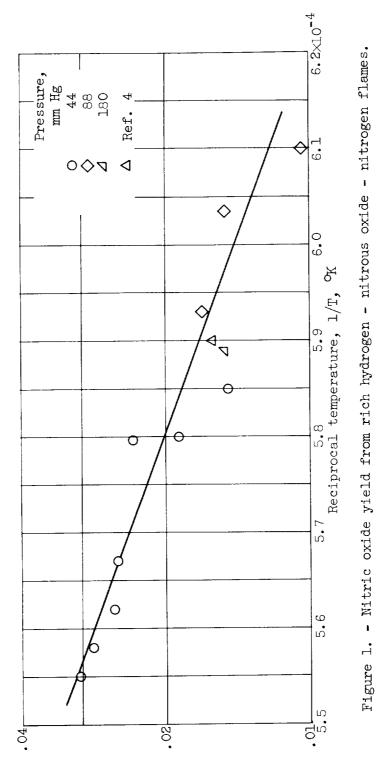
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TABLE I. - DATA FOR FUEL-RICH FLAMES

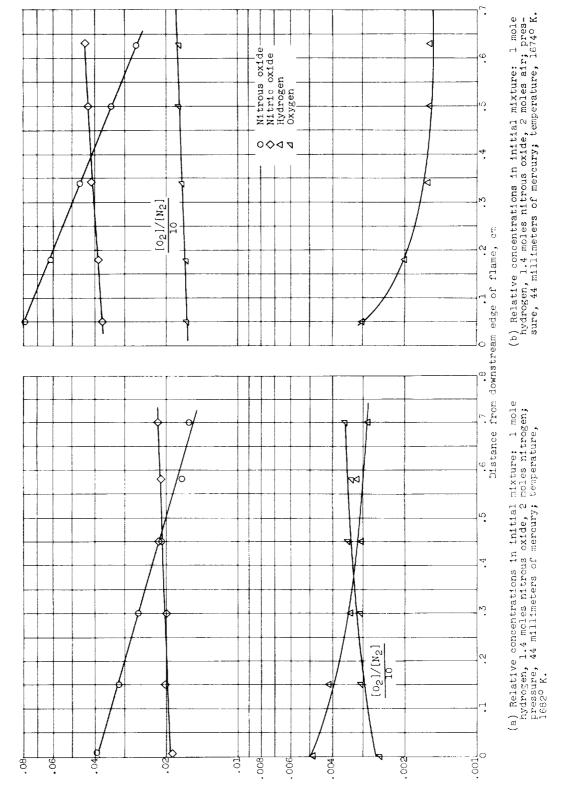
Pres- sure, mm Hg	Temper- ature,	Volume pres	Nitric oxide		
	I	Hydro- gen	Nitrous oxide	Nitro- gen	yield, [NO] [N2O]
44	1800 1779 1763 1796 1728 1716	61 70.6 58.0 65.7 52 47.5 81.1	50.5 50.5 44.5 50.5 40 38 50.5	72.2 72.2 63.0 72.2 56.7 56.7 72.2	0.0309 .0258 .0252 .0285 .0233 .0152 .0146
88	1689 1660 1643	65.7 56.6 81.1	50.5 44.5 50.5	72.2 63.6 72.2	0.0168 .0157 .0104
180	1700	75	68	115	0.0151

TABLE II. - DATA FOR FUEL-LEAN FLAMES

Pres- sure, mm Hg	Diluent	Temper- ature,	Volume pres	flow at	l atm /sec	Nitric oxide	Mole fraction of hydro-	Mole frac- tion of oxygen	$-\frac{d \ln[N_20]}{dt},$	Oxygen atom concentra-
, an 115			Hydro- gen	Nitrous oxide	Diluent	[N <sup>5</sup> 0]	gen		sec-l	[0], moles/liter
22	Nitrogen	1606 1615 1663 1688 1685	15.8 15.8 20 23 22	22.9 22.9 28 32.2 31.9	28 33.3 40 46 38.5	0.049 .052 .063 .066 .068	8.5×10 <sup>-3</sup> 9.7 8.8 11.2 8.6	0.016 .014 .018 .018 .025	418 589 697 925 846	2.4×10 <sup>-7</sup> 2.5 2.8 3.5 3.5
	Air	1562 1598 1708	20 23 32.2	28 <b>32.2</b> 44.5	40 46 63.6	0.104 .115 .132	3.8 3.4 5.4	0.093 .096 .097	353 570 2532	7.2 6.9 8.9
44	Nitrogen	1682 1795 1828 1719 1738 1634 1776 1692 1751	20 32.2 36.1 25 25 15.8 32.2 22.0 32.2 32.0	28 44.5 50.5 35 35 22.9 50.5 36.7 38.0 54.5	40 63.6 72.2 43.7 52 28 63.6 63.6 63.6 63.6	0.049 .066 .070 .054 .058 .035 .074 .062 .054	2.1 3.2 3.4 2.6 2.8 1.8	0.024 .027 .029 .027 .026 .020 .040 .027 .016	247 899 1208 449 419 153	1.8 2.8 3.2 2.4 2.4 1.3
	Air	1674 1782 1804 1717 1635	32.2 45 50 36.1 28.4	44.5 63 70 50.5 39.2	63.6 90 100 72.2 54.5	0.087 .110 .117 .093 .080	0.92 1.8 2.1 1.1	0.109 .110 .110 .110 .098	485 2110 2227 907 295	3.5 6.5 7.3 4.0 3.8
88	Nitrogen	1736 1700 1862	36.1 32.2 53.1	50.5 44.5 74.5	72.2 63.6 106.2	0.052 .047 .063	0.68 .74 1.2	0.031 .029 .032	328 272 1672	1.4 1.5 2.4
	Air	1707 1762	50 60	70 84	100 120	0.090	0.48 .58	0.114	646 900	3.6 4.2
180	Nitrogen	1748 1816 1895 1907 1950	57.3 75 100 100 120	80.3 105 140 140 168	114 150 160 200 240	0.049		0.025 .035 .032 .030 .023	510 1180 2450 2260 4050	
44	Argon	1885 175 <b>3</b>	32.2 20	44.5 28	63.6 41	0.076 .056	4.8 3.3	0.029 .025	2790 976	5.9 3.7



Concentration of nitric oxide telaconcentration,  $\left[ \text{NO} \right] / \left[ \text{N}_{2} \text{O} \right]_{0}$ 

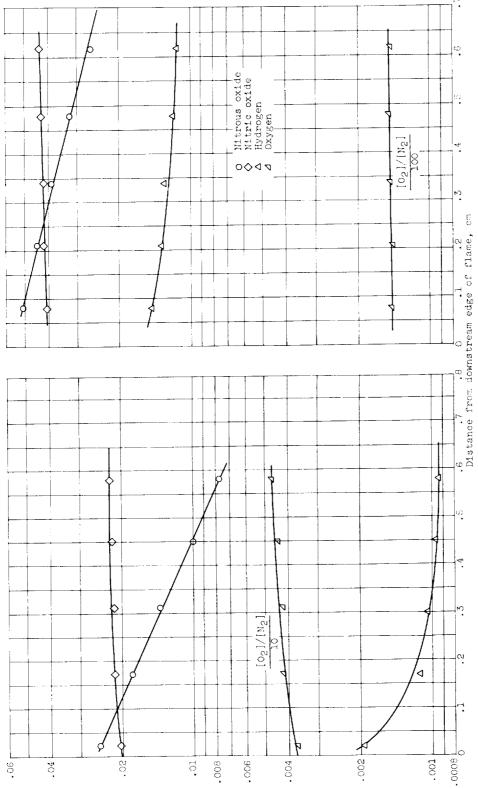


Concentration relative to nitrogen

(d) Relative concentrations in initial mixture: I mole hydrogen, 1.4 moles nitrous oxide, 2 moles air; pressure, 22 millimeters of mercury; temperature, 1562° K.

Figure 2. - Sampling profiles downstream of lean flames.

(c) Relative concentrations in initial mixture: 1 mole hydrogen, 1.4 moles nitrous oxide, 2 moles nitrogen; pressure, 88 millimeters of mercury; temperature, 1736 K.



Concentration relative to mitrogen

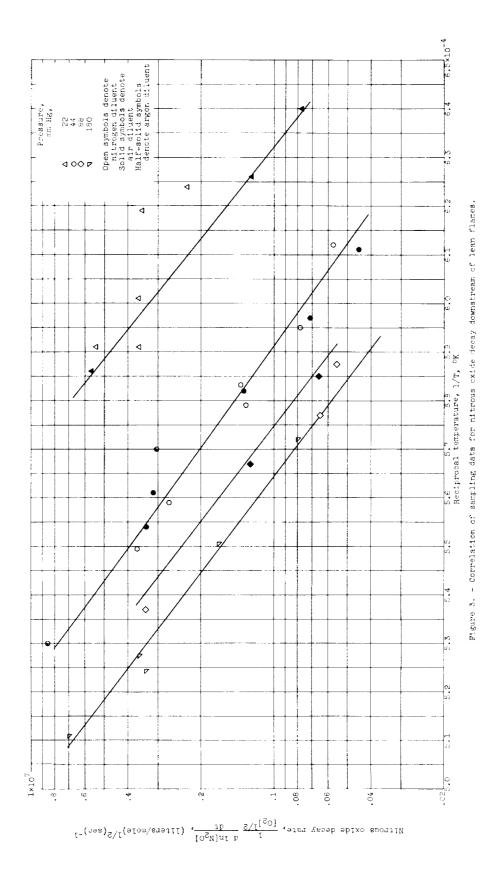
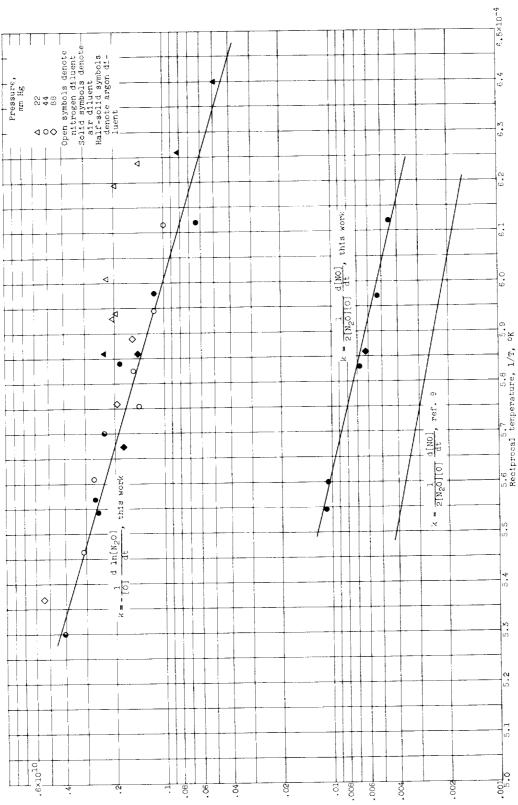


Figure 4. - Correlation of sampling data in terms of measured oxygen atom concentration.



Aeaction-rate constant, k, (liters/mole)(sec).

